Effect of Deflocculants on High Alumina Low Cement Castables

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BY

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CERTIFICATE

This is to certify that the thesis entitled, "Effect of Deflocculants on High Alumina Low Cement Castables" submitted by Mr. Aditya Pratap Dhall Samant, 111CR0551 in partial fulfilment for the requirements for the award of Bachelor of Technology degree in Ceramic Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in this thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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ABSTRACT

Refractories are an integral part of iron and steel making industries, and they face challenging operational parameters at elevated temperatures. Hence, there has been a shift of focus towards unshaped refractories, over conventional and shaped refractories. Refractory castables consists of a mixture of aggregate refractory grains, matrix phases, binders, deflocculants and other additives. In order to get the optimum result as envisioned, castable manufacturing needs to be controlled right from compositional batch calculation to the firing process. In this project, the effect of different types of deflocculant and its amount on high alumina low cement castables is observed. As the flowability is dependent on the particle size distribution and packing of the castable system, the particle size ranges follow a continuous distribution approach based on Dinger-Funk equation. The work studies for a distribution coefficient of q=0.21, which lies in the self-flowable castable zone. To determine the physical and mechanical properties, castable sample blocks are casted in a pre-fixed mold and subsequently dried and fired at two different temperatures namely, 900 °C and 1500 °C. The dimensional measurement and Cold Crushing Strength was observed at each step. Thus, the Bulk Density, CCS, Flowability values and XRD of different batches were analysed and discussed. The varying effect of different deflocculants were noted.

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LIST OF ABBREVIATIONS

Sl. No.	Abbreviation	Full form
1.	HAC	High Alumina Cement
2.	PSD	Particle Size Distribution
3.	XRD	X-Ray Diffraction
4.	WTA	White Tabular Alumina
5.	WFA	White Fused Alumina
6.	CPFT	Cumulative percent finer than
7.	BD	Bulk Density
8.	CCS	Cold Crushing Strength
9.	CA	CaO.Al2O3
10.	CA2	CaO.2Al2O3
11.	CAH10	CaO.Al2O3.10H2O
12.	C2AH8	2CaO.Al2O3.8H2O
13.	C3AH6	3CaO.Al2O3.6H2O
14.	C12A7	12CaO.7 Al2O3

CHAPTER 1
INTRODUCTION

1. Introduction:

Ceramic technology is a modern, dynamic and diversified field having its roots in ancient technology that is more than 24000 years old. Amongst different classes of ceramics, refractories are materials whose chemical and physical properties makes them applicable to structures or as components of system that are exposed to environment of above 1000 ^{0}F [as per ASTM nomenclature, 1984]. Hence, Refractories are required to have specific properties like high temperature withstandability, strength at elevated temperature and corrosive atmosphere resistance depending upon the application.

Refractories constitute discontinuous large sized aggregates (filler) phases and a continuous fine binder phase in the matrix. They are divided into two categories namely, Shaped and Unshaped (Monolithics) refractories.

Application of refractories in various industries includes:

- Glass Industry
- Iron and Steel Industry
- Cement Industry
- Petro Chemical Industry
- Aluminium Industry
- Oil Industry

Unshaped or Monolithic refractories have gained popularity over shaped refractories as their installation is easier and cheaper, they are single cast piece that can take any shape of the equipment, they have lower amount of lining joints hence low corrosion susceptibility, better volume stability and good spalling resistance. These properties make it very useful in iron and steel industries to satisfy various operational parameters at high temperature.

Most castables are based on Calcium Aluminate Cements. Refractory castables are primarily a composition of refractory grains, matrix components, bonding agents and additives. The composition of each component is varied to get desirable properties. The commonly used hydraulic binders are Calcium Aluminate Cement, but the presence of CaO results in low melting phases of Alumina refractory. The dehydroxylation reactions need to be carefully controlled as they possess the explosive ability.

Castables are classified in accordance to IS: 10570 as follows:

1) Conventional: A castable containing having calcium oxide content greater than 2.5% on calcined basis.
    a. Dense castable
    b. Insulating castable: B.D. has a maximum value of 1.85 g/cc
2) Low cement castable (LCC): calcium oxide content in between the range of 1% to 2.5% on calcined basis.
3) Ultra low cement (ULCC): calcium oxide content in between the range of 0.2% to 1% on calcined basis.
4) No cement castable (NCC): calcium oxide content maximum of 0.2% on calcined basis.

Although conventional castables having a large amount of cement content are a major share of those produced, the use of low cement varieties like LCC's and ULCC's have grown significantly in last couple of years. The presence of CaO in cement depreciates its high temperature properties. To prevent this in recent times Low Cement castable (LCC) composition is being preferred which has CaO content between 1-2.5%.

Castables are of two types namely, Self-flow castables and Vibratable castables. Self-flow castables contain a greater amount of fines so, they flow under their own mass while, and vibratable castables containing lesser amount of fines require the application of external load or vibration to take shape. Usually the castable tends to be self-flowing in nature if the distribution coefficient (q) is less than 0.25 ,and tends to be vibratable if the distribution coefficient is more than 0.25. In order to keep the slurry flowable and dispersed, deflocculants are added which prevent agglomeration and improve packing density. Higher the amount of binder, higher is slurry flowability, hence betters packing and better physical and mechanical properties obtained. But too high flowable mass may indicate higher sphericity of particles, resulting in lower strength, which is not desirable for the refractory application. Hence the choice of refractory castable composition must be taken among the deflocculants giving most optimum properties for appropriate amount.

CHAPTER 2
LITERATURE REVIEW

2. Literature Review:

2.1. Refractory Cements:

Refractory cement contain various mineralogical phases of Calcium aluminate. These phases are C_3A, CA, CA_2 and CA_6. The major constituent is C_3A. The major hydraulic phase is CA. various chemical and physical changes take place upon hydration. On the application of heat hydrates break down to leave reactive products that recrystallize and form a network of sintered material at lesser temperature than would have required for sintering the powder. Hence, the nature of hydrates formed their physical characteristics and affinity to react will play an important role in determining the properties of fired cement.

Upon addition of water, CA/CA_2 hydrolyses and when super-saturation occurs the hydrates begin to nucleate and grow, allowing more anhydrous CA/CA_2 to dissolve in the solution. As a consequence, a strong inter-locking microstructure of hydrate crystals is obtained. CA_2 is less reactive than CA.

$C_{12}A_7$ hydration is a lot faster so, it effectively flash sets. Thus the strength of unheated hydrates depends mostly on its density and type of bonding among crystals [4].

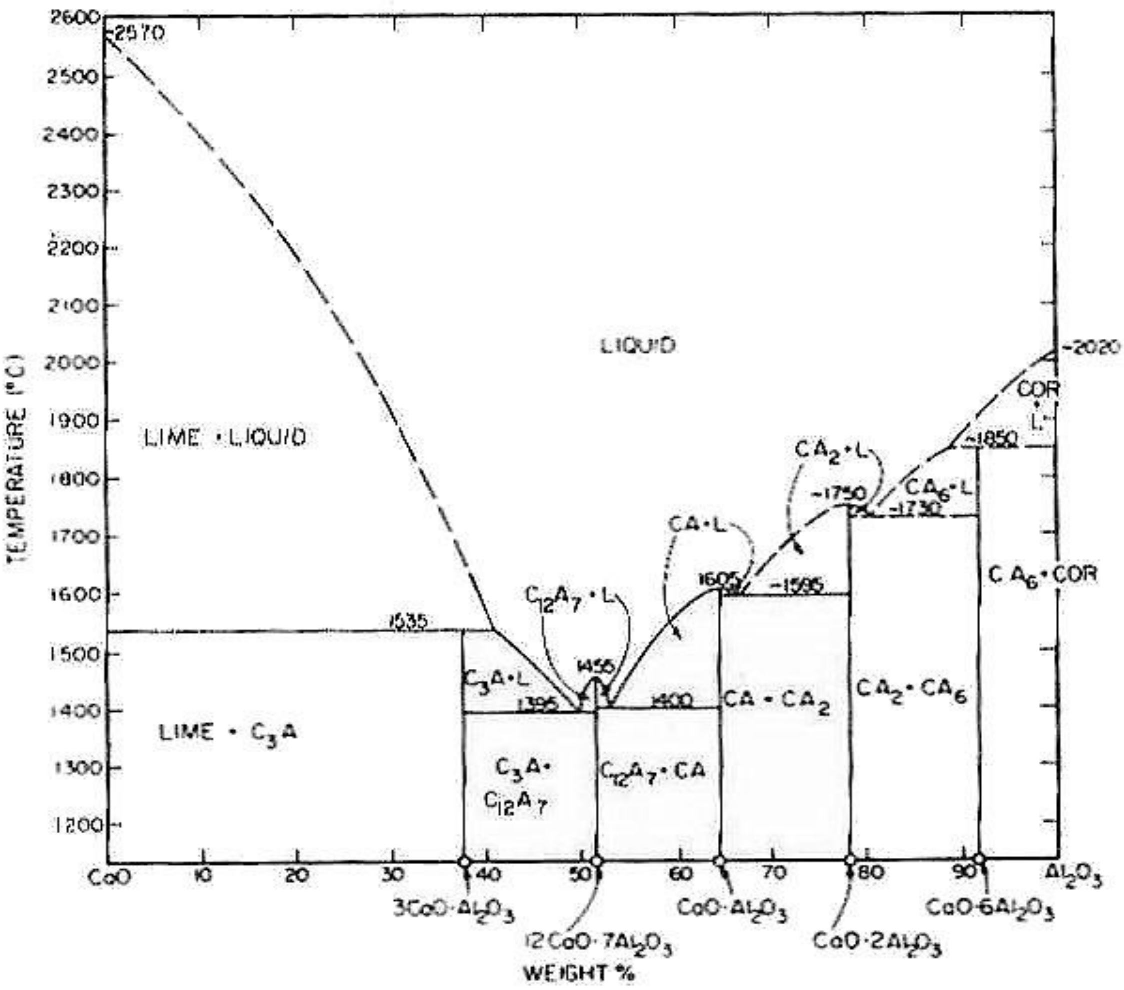

Figure 1: CaO-Al_2O_3 Phase Diagram [10]

2.2. **Monolithics**:

The term monolithic is a combination of two words namely, 'mono' which means single and 'lithus' which means stone. It comprises of aggregate refractory grains (filler phase), binders which form the matrix phase (finer phase) and additives like deflocculants and anti-setting agents. Upon addition of water these materials tend to harden into a solid mass. The primary reason for the rise in popularity of monolithics in comparison to shaped refractories, is its easy availability, quicker and cheaper installation, and low amount of corrosion susceptible joints and good dimensional stability [11, 12].

2.3. Castables:

They are unshaped refractories which are pre-requisites to produce monolithic products. The primary motive is to obtain materials having high refractoriness and low corrosion properties. A low content of CAC allows to minimise water content required for hydraulic bonding and subsequently obtaining low porosity after drying. The nature of particle distribution also plays a major role. A continuous PSD containing finer particles increase the flowability of the castable. Flowability is also dependent on water content and nature and amount of deflocculants.

On the basis of flow characteristics castables are sub-divided into Self-flow castables and Vibratable castables. Self-flow castables contains greater amount of fines so, they flow under their own mass while, and vibratable castables containing lesser amount of fines require the application of external load or vibration to take shape [1].

2.4. Particle Size Distribution:

Particle packing involves two types of approach namely, discreet approach and continuous approach. All particle sizes in the range of a discrete approach are not represented but, contains a lesser number of defined, discrete particle sizes. Its disadvantages are it doesn't consider the option of stirring a system after it has been packed. The particles are packed consistent with the theory only when they are packed one at a time in a coarser to finer fashion.

A continuous distribution approach involves that all possible particle sizes within a range are represented. Being consistent with the similarity condition, Andreasen proposed a continuous distribution equation,

$$\frac{CPFT}{100} = \frac{D^q}{D_L^q}$$

Where,

CPFT denotes Cumulative percent finer than,

D denotes the particle size of which CPFT is calculated,

D_L denotes the maximum particle size, and

q denotes the distribution coefficient.

But the shortcomings of the equation were that it did not involve a minimum particle size, so the restriction of particle sizes to the available range was not possible. By modifying Andreasen's theory, the Dinger-Funk distribution equation formulates to add a smallest particle size (D_s) variable in order to restrict the minimum size.

$$\frac{CPFT}{100} = \frac{D^q - D_s^q}{D_L^q - D_s^q}$$

Where,

D_s denotes the minimum particle size,

Packing needs to be optimum as it leads to castables requiring a minimal amount of water for setting, whch implies less porosity, which will give a higher packing density. Thus the castable will have improved physical properties. The flow characteristics of castable is self-flowing in nature if 'q' is less than 0.25 else it is vibratable in nature. Lower the q-value greater the amount of fines in the batch implying greater flowability [6].

2.5. Reactions involved in firing castables:

The castable composition contains CAC binder. CAC has major phases CA and CA_2 in it. These phases hydrolyse when they come in contact with water.

$$CA + H_2O \xrightarrow{<18^0C} CAH_{10}$$

$$CA_2 + H_2O \xrightarrow{<18^0C} CAH_{10}$$

Upon temperature application, these phases start to lose water.

$$CAH_{10} \xrightarrow{22-35^0C} CAH_8 + AH_3$$

$$CAH_8 \xrightarrow{>35^0C} C_3AH_6 + AH_3$$

C_3AH_6 is the main hydrate phase. As temperature increases, dihydroxylation process continues. Between temperature 300-700 °C, all hydraulic bond may decompose and complete loss of crystallisation water may occur.

$$C_3AH_6 \xrightarrow{300-700\ °C} C_{12}A_7$$

Therefore, castables show characteristics strength drop at intermediate temperatures (550-950 °C).

At temperature above 900 °C calcium aluminates react with fine alumina and matrix components.

$$C_{12}A_7 + A \xrightarrow{>900\ °C} CA$$

$$CA + A \xrightarrow{>1400\ °C} CA_2$$

At this temperature sintering occurs and this gives mechanical and physical strength.

CA may also react with fume silica to form Anorthite.

$$CA/CA_2 + S \xrightarrow{>1400\ °C} CAS_2$$

Here, C denotes CaO; A denotes Al_2O_3; S denotes SiO_2; H denotes H_2O

CHAPTER 3
EXPERIMENTAL

3. Experimental:

3.1. Objective:

The aim of the project is to study the effect of different deflocculants on various properties of High Alumina Low Cement Castable.

Three different types of deflocculants with 2 different amounts were studied for various properties.

3.2. Batch calculation:

Raw materials used,

Coarse aggregates: White Tabular Alumina (WTA), White fused alumina (WFA)

Fine aggregates: WTA fines/Reactive Alumina

Binder: High alumina cement (HAC)

Size fraction(in mm)	**Raw Material**
3 mm to 2 mm	White Tabular Alumina
2 mm to 1 mm	White Tabular Alumina
1 mm to 0.5 mm	White Tabular Alumina
0.5 mm to 0.3mm	White Fused Alumina
0.3 mm to 0.1 mm	White Fused Alumina
0.1 mm to 0.001 mm	Calcined Alumina, high alumina cement, fume silica

Table 1: List showing the size fractions and the corresponding raw material

For a distribution coefficient (q) value of 0.21 and total Batch weight of 1200 gms.

Serial no.	**Alumina in mm (Mesh size)**	**%**	**Weight (gm)**
1	3-2	10.03	120.36
2	2-1 (8/14)	15.29	183.48
3	1-0.5 (14/28)	13.21	158.52
4	0.5-0.3 (28/48)	8.58	102.96
5	0.3-0.01 (-48)	38.67	464.04
6	0.01-0.001	5.22	62.64
7	HAC	4	48
8	Fume silica	5	60
	Total	= 100	= 1200 gms

Table 2: List showing various raw material size ranges and amount taken, for batch q=0.21

3.3. Composition details of 6 Batches:

Along with castable batch composition three different types of deflocculants were added in two amounts. The amount of Deflocculant used is in percentage of total batch weight.

<table>
<tr><td>Batch</td><td>Deflocculant used</td><td>Chemical name</td><td>Amount used (%)</td></tr>
<tr><td>D-C 0.3</td><td rowspan="2">Darvan-C</td><td rowspan="2">Ammonium Polymethacrylate</td><td>0.3</td></tr>
<tr><td>D-C 0.5</td><td>0.5</td></tr>
<tr><td>Shmp 0.3</td><td rowspan="2">SHMP</td><td rowspan="2">Sodium Hexametaphosphate</td><td>0.3</td></tr>
<tr><td>Shmp 0.5</td><td>0.5</td></tr>
<tr><td>A 0.3</td><td rowspan="2">ADS + ADW</td><td rowspan="2">Alumina Dispersed Summer + Alumina Dispersed Winter</td><td>0.3 + 0.3</td></tr>
<tr><td>A 0.5</td><td>0.5 + 0.5</td></tr>
</table>

Table 3: List showing deflocculants used and the amount of it in different batches

3.4. Flow sheet of Process:

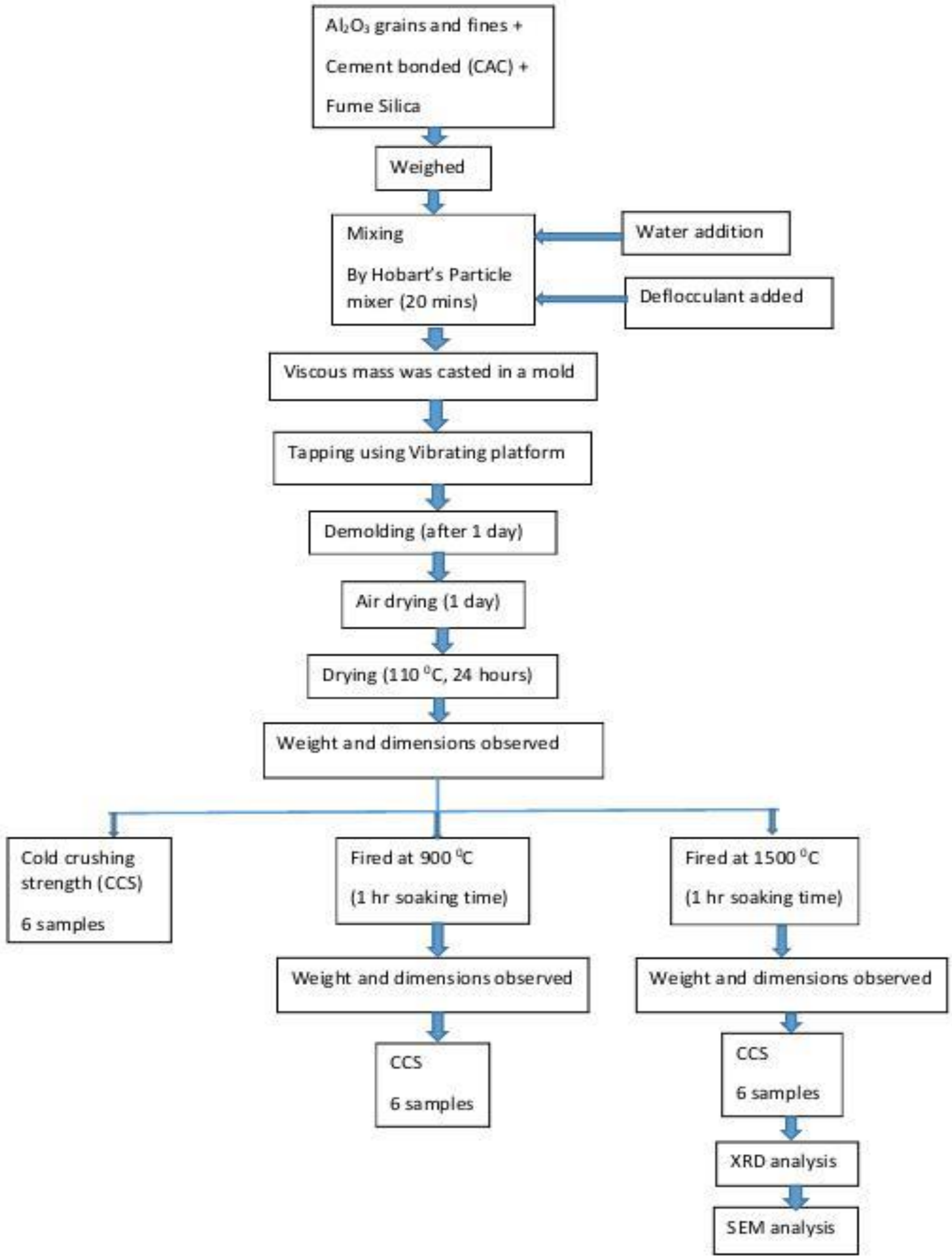

Figure 2: Process Flowsheet

3.5. Procedure:

The observations were noted with 3 different types of deflocculants, namely Darvan-C, SHMP and ADS-ADW. All 3 deflocculants were taken at 2 different weight% of total weight of the mixture. Various observations for each of the 6 type of batch was taken.

- The batch composition was weighed as calculated and then stirred in a Hobart’s Particle mixer for 20 minutes, along with water (7%) and deflocculant addition.
- The slurry mass obtained was casted in a pre-fixed mold. Then it was settled and densely packed using a vibrating platform.
- The flowability values were checked using a Flow cup of inner base diameter 100 mm, for 30 sec vibration.
- The samples in the mold were kept casted for one day and then demolded.
- Then air drying was done for atleast two days. Then it was placed in the drier at 110 C for 24 hours.
- After that the weight and dimensions of the samples were noted for density calculation.
- Then the CCS of a sample from each batch was measured.
- Then one sample from each batch composition was taken and all of the 6 samples were fired at 900 C for a soaking time of 1 hour. After that, the weight and dimensions of the samples were noted for density calculation. Then the CCS of samples were measured.
- Then another one sample from each batch composition was taken and all of the 6 samples were fired at **1500 C** for a **soaking time of 1 hour**. After that, the weight and

dimensions of the samples were noted for density calculation. Then the CCS of samples were measured.

- After observing the CCS values, the finer powder particles from the castables were taken. These fine powders were further grounded using mortar and pestle. Then they were analysed for constituent phases by **X-ray Powder Diffraction** method.

- The position ($^{0}2\theta$) range in which the analysis was done, **20^{0}-60^{0}** and the rate was **10^{0}/min**. The intensity vs position data was obtained for each of the 6 samples. The data was analysed using **X'Pert HighScore** and phases were identified by tallying them with **JCPDs** file data. The graphs were plotted and the phases obtained were discussed.

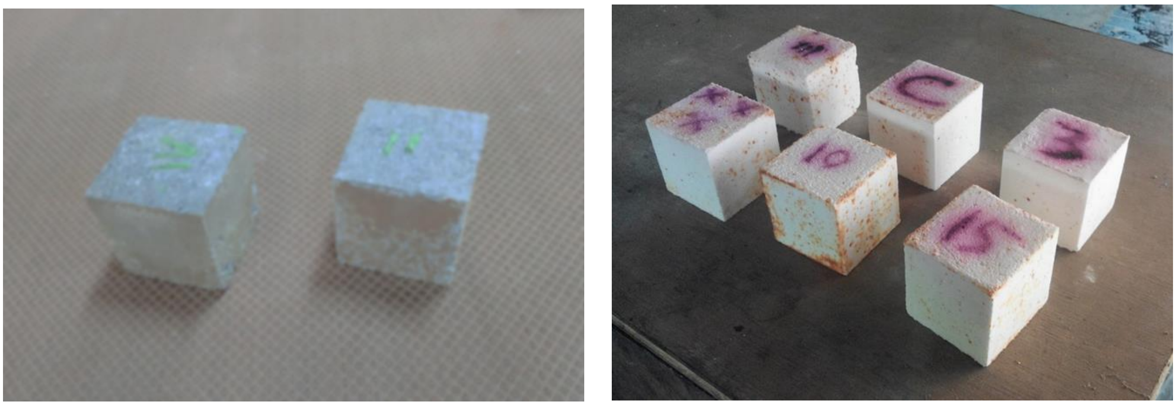

Fig 3: Unfired Castables and Castables fired at 1500 °C

Fig 4: Hobart's Particle Mixer and Mold

Fig 5: Flow cup

Fig 6: Close-up of the castable during mixing

Fig 7: 30 seconds of vibration brings the mass to flow out of its initial edges. Vibrational flowability value is measured.

CHAPTER 4
RESULTS & DISCUSSIONS

4. Results and Discussions:

4.1. Particle Size Distribution(PSD):

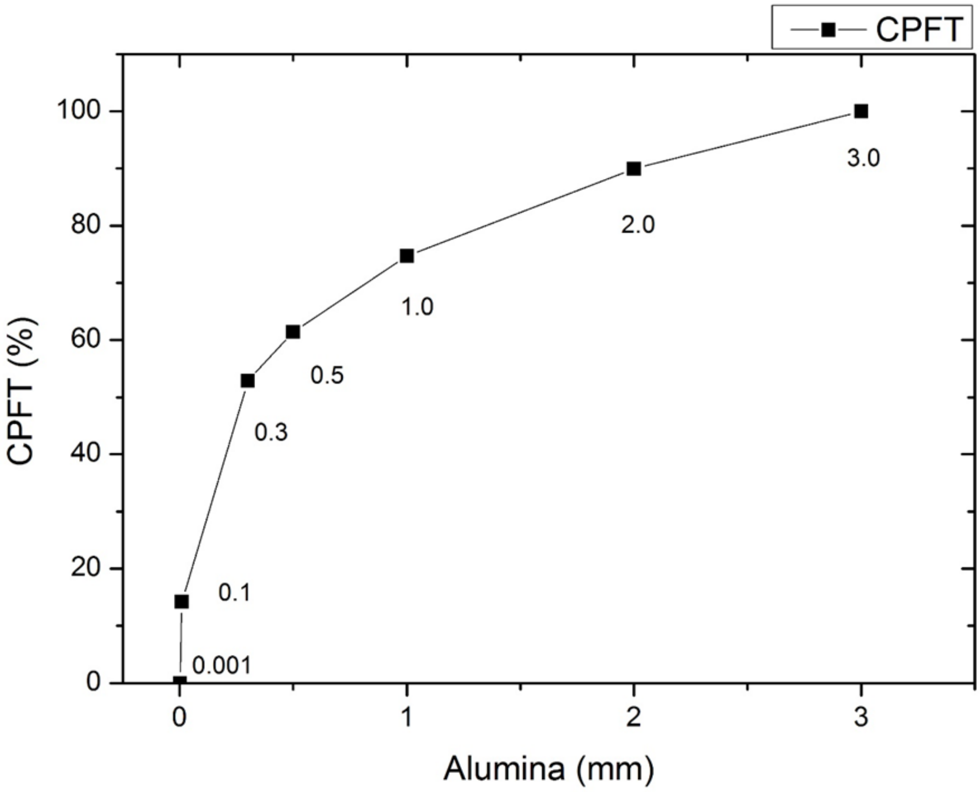

Figure 8: Plot of CPFT v/s PSD in mm for q value 0.21

The figure shows the plot of CPFT with the PSD, with the value of **q= 0.21**. The highest particle size is 3 mm which shows 100% CPFT and the lowest particle size is 1μm which shows 0% CPFT. There is a gradual decrease in the slope with reducing particle size range, as a percentage of particles finer than that decreases. There is a sudden change in the slope of the plot at 0.3 mm fines due its high content (38.67 %).

This plot follows Dinger-Funk distribution equation for a distribution coefficient q of 0.21.

4.2. Flowability Value:

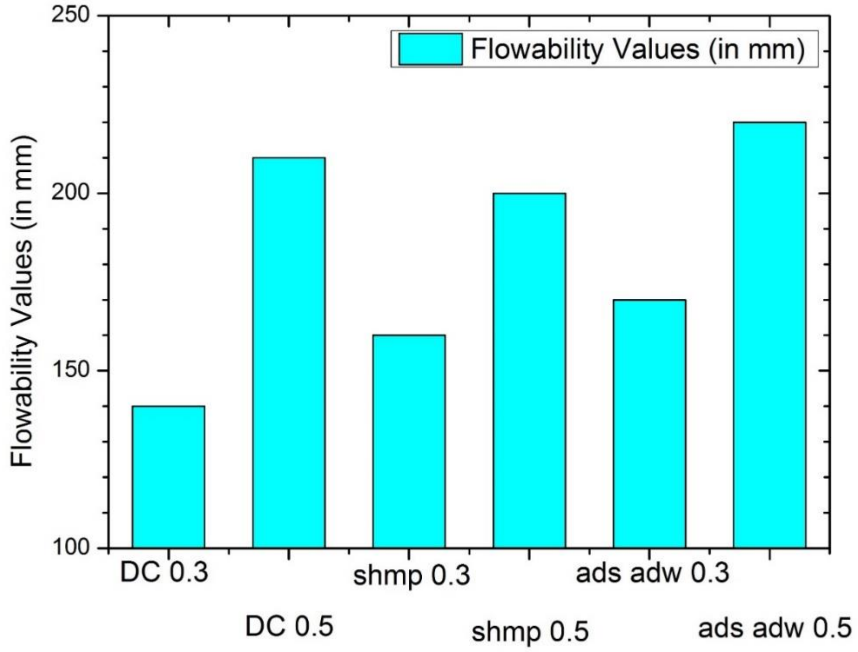

Figure 9: Plot of Flowability values w.r.t. different batches

It is observed that with higher the Deflocculant content, the flowability of slurry increases. As the amount of water added was equal ~7%, the flowability values can be compared to show that ADS ADW deflocculated castable had higher flowability.

4.3. Bulk Density (BD) (in g.cm^{-3}):

Temp ◦C	Darvan-C 0.3	Darvan-C 0.5	SHMP 0.3	SHMP 0.5	ADS ADW 0.3	ADS ADW 0.5
110	2.77	2.80	2.77	2.83	2.76	2.85
900	2.75	2.79	2.77	2.85	2.75	2.79
1500	2.86	2.87	2.89	2.95	2.85	2.94

Table 4: List of BD of batches w.r.t. temperature

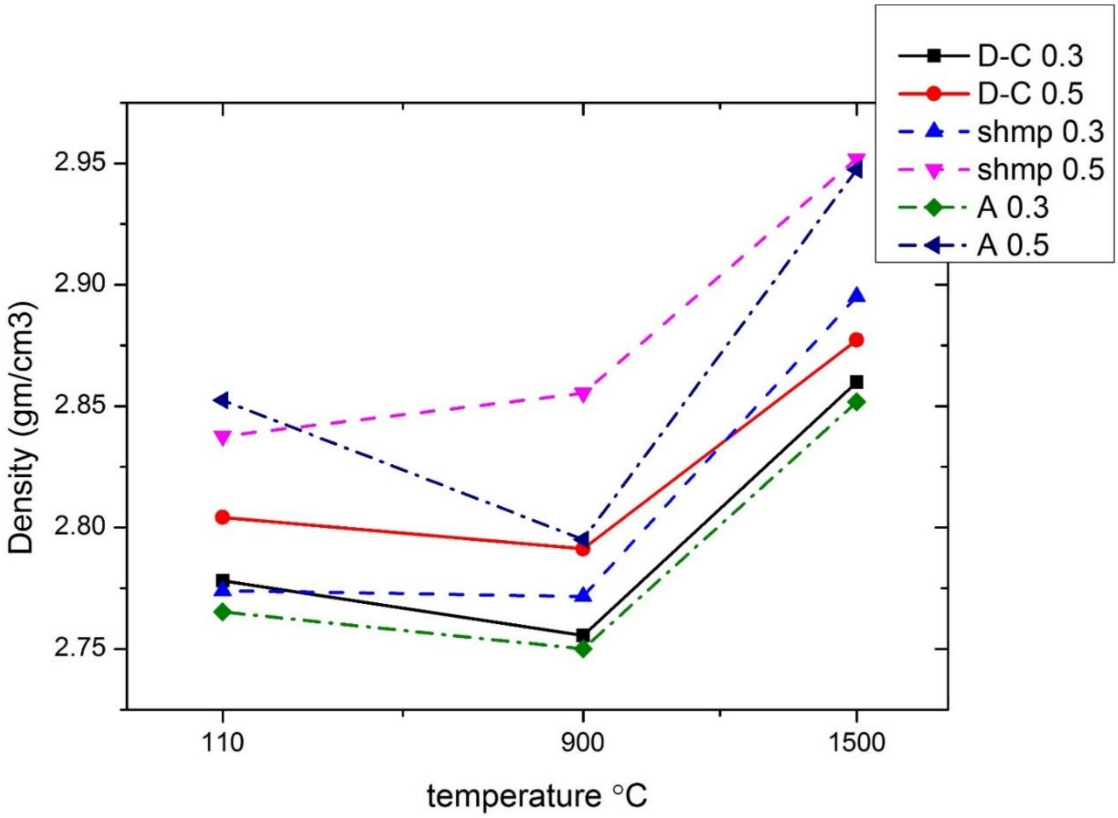

Figure 10: Plot of Density v/s Temperature

The study is done by measuring the dimensional density of samples of each of the 6 batches. It is observed that with higher Deflocculant content, the flowability of slurry increases. Hence better packing during casting leads to higher Bulk Density.

At **900 °C** there is a decrease in BD as around that temperature completion of bond rupture of CAH bonds takes place, which leads to complete loss of chemically bonded water and formation of void spaces, which in turn reduce density.

At **1500 °C** due to sintering and formation of CA2, a dense body is obtained.

SHMP 0.5 wt% and ADS ADW 0.5 wt% show good BD.

4.4. Cold Crushing Strength (CCS) ((in MPa):

Temp ◦C	Darvan-C 0.3	Darvan-C 0.5	SHMP 0.3	SHMP 0.5	ADS ADW 0.3	ADS ADW 0.5
110	25.00	29.00	27.00	31.00	27.40	37.24
900	39.92	44.40	34.20	49.92	41.32	56.60
1500	76.00	80.12	65.60	67.44	118.68	144.56

Table 5: List of CCS of batches w.r.t. temperature

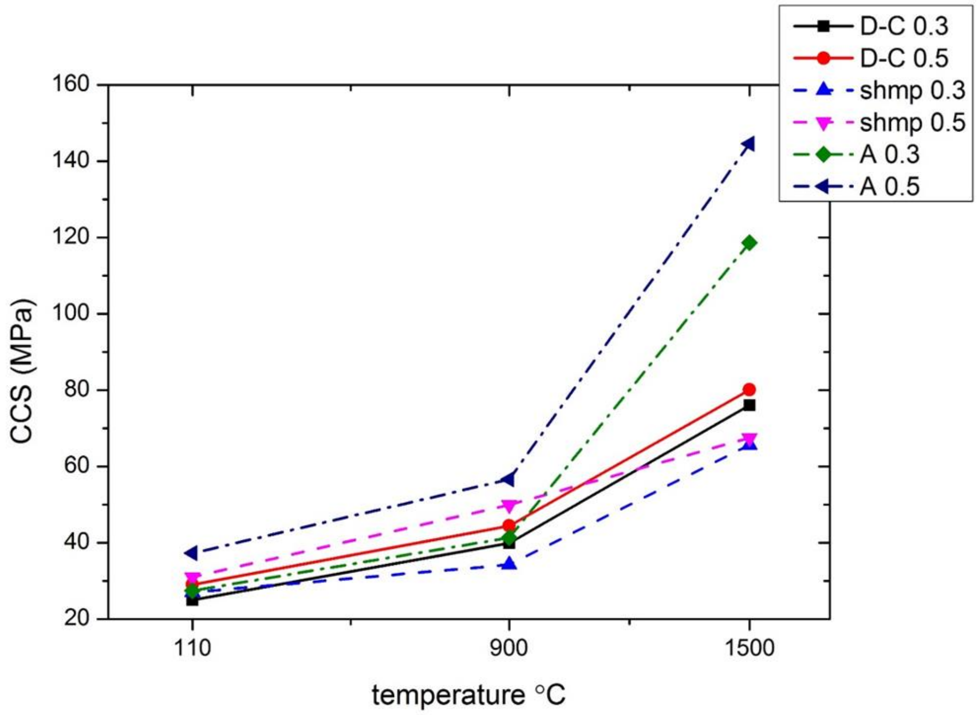

Figure 11: Plot of CCS v/s Temperature

The study is done by determining the CCS of samples of each of the 6 batches at varying temperature. It is observed that with higher Deflocculant content, CCS strength also increases, as a denser body is formed. Also the samples show relatively high CCS value at higher temperature (1500 °C) as sintering has occurred. ADS ADW 0.5wt% composition sample shows the highest CCS value.

4.5. X-Ray Diffraction:

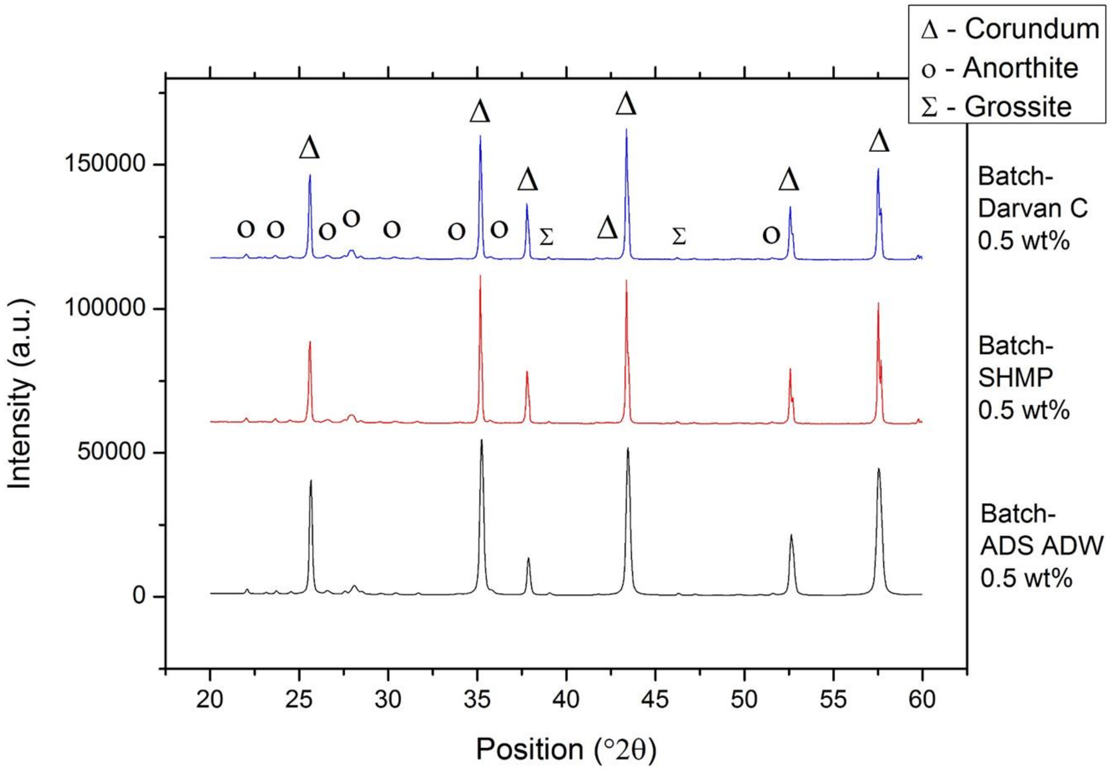

Figure 12: Plot of XRD at Intensity v/s Position (°2θ) for 3 batches

The major phase present is Corundum (Alumina). The other phases present is Anorthite ($CaO.Al_2O_3.2SiO_2$), which is obtained by the following reaction,

$$CA/CA_2 + SiO_2 = CAS_2 \text{ (Anorthite)}$$

The other phase present is Grossite [CaO(Al2O3)$_2$] may be obtained due to the reaction between CA phase present in the Cement Binder (CAC) used and fine alumina.

$$CA + A = CA_2$$

The deflocculants are mostly organic based materials and are used in a very low percentage in the composition, hence they do not affect the XRD analysis in a major way. Here, C denotes CaO; A denotes Al_2O_3; S denotes SiO_2 and H denotes H_2O.

CHAPTER 5
CONCLUSION

5. Conclusion:

- Thus it is observed that the batch composition is containing **ADS ADW 0.5wt%** gives a denser body and also a high Cold Crushing Strength (CCS).
- The plot of CPFT vs PSD, with the value of **q= 0.21** undergoes a sudden change in the slope of the plot at 0.3 mm fines due its high content.
- It is observed that with higher Deflocculant content, the flowability of slurry increases.
- The density of Samples decreases after firing at around 900 ^{0}C, may be due to formation of void spaces after complete loss of crystalized water but, it reaches the highest level at 1500 ^{0}C as sintering has already occurred by this temperature leading to filling up of void spaces.
- The reaction between $CaO.Al_2O_3$ and fine alumina forming only $CaO.2Al_2O_3$ are the reason for high strength development at higher temperatures.
- The phases present in the castable matrix is Corundum, Anorthite and some amount of Grossite.
- Both self-flowing and vibratable castables are designed and fabricated using controlled particle size distribution at required theoretical distribution coefficients. This study shows improved characteristics of the products that is used for practical applications.

CHAPTER 6
REFERENCE

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